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THE EFFECT OF MINERALIZING ADDITIVES ON SYNTHESIS OF CERAMIC PIGMENTS BASED ON NATURAL WOLLASTONITE

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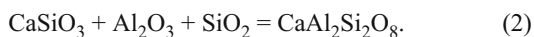
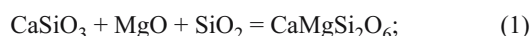
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The mineralizing effect of additives of natural fluorine-bearing mineral topaz and boric acid on the synthesis of ceramic pigments with the diopside and anorthite structures based on natural wollastonite is studied. The brightest color range is obtained at 1100°C. It is established that topaz has obvious advantages over the traditional mineralizer, i.e., boric acid. The obtained ceramic pigments have good chromophore properties, are resistant at high firing temperature, and can be extensively used in ceramic production.

Mineralizers have an important role in the production of ceramic pigments. They improve by 93% the color characteristics of pigments and lower the temperature of synthesis. Mineralizers have a significant effect on the crystal lattice of sintering material and on the properties of its liquid phase. The essence of the mineralizing mechanism is loosening the crystal lattice in melting and bringing it to an active state [1]. The presence in the reaction mixture of an agent that forms a relatively low-melting mixture with one of several batch components contributes to increasing the contact area between the reactants and intensifying the diffusion rate and the entire process. It is established that to intensify numerous reactions in the solid phase, the content of mineralizer should not exceed 1 – 3% of the total weight of the mixture.

Mineralizing agents used for producing ceramic pigments are compounds of boron, fluorine, and alkali metal oxides. The effect of mineralizing additives is especially significant in the synthesis of ceramic pigments based on natural minerals. Considering that the ionic capacity of natural minerals is relatively low, pigments based on them have less bright coloring than those synthesized from pure oxides and metal salts. To intensify the brightness of pigments, mineralizing additives have to be added.

We have investigated the mineralizing effect of additives of natural fluorine-bearing mineral topaz and the traditional mineralizer (boric acid) on the synthesis of ceramic pigments with the diopside and anorthite structure based on natural wollastonite according to the following reactions:



The crystal structure in the course of its rearrangement is capable of a more intense absorption of colorant ions. Mine-

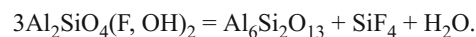
ralizers intensify this capacity by stimulating the formation of the liquid phase, creating artificial crystallization centers, and forming solid solutions.

Boric acid H_3BO_3 heated to 100°C becomes dehydrated and transforms into metaboric acid HBO_2 . Further heating leads to the formation of vitreous B_2O_3 , its crystallite modification has a melting point of 450°C and a boiling point of 2250°C. All oxides except for BeO , Al_2O_3 , ZrO_2 , and TiO_2 dissolve well in melted B_2O_3 ; which intensifies the reactions of synthesis with the participation of the liquid phase.

The positive effect of B_2O_3 on the chromophore properties of pigments is manifested in many cases. It is known that the main chromophores are transition metal ions: Co^{2+} , Ni^{2+} , Fe^{2+} , Cr^{3+} , and V^{3+} . They have an incomplete electron shell and a high polarizing capacity. Their tint varies depending on the polarization of the ion, particularly, oxygen, which makes up part of the ion complexes of transition metals: $[\text{CoO}_4]$, $[\text{CoO}_6]$, $[\text{NiO}_4]$, $[\text{NiO}_6]$, $[\text{CrO}_4]$, etc. The cations in the specified complexes polarize the anion by shifting the pigment absorption spectrum toward the visible range. The polarizability of the anion in the specified complexes grows in the presence of B^{3+} ; consequently, the absorption band in the visible spectrum range intensifies [1].

Thus, boric compounds, on the one hand, facilitate the transition of crystal compounds to an active state without destroying them and, on the other hand, intensify the chromophore properties of pigments.

As topaz is heated from 850 – 900 to 1200°C, fluorine is removed in the form of silicon fluoride SiF_4 , and after firing at 1500°C topaz constitutes virtually pure mullite [2]:



It is observed that the presence of fluorine improves the reaction capacity of the crystal lattice of the material due to the loosening of its silicon-oxygen skeleton and decreasing

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TABLE 1

Material	Mass content, %							
	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	Fe ₂ O ₃	P ₂ O ₅	calcination loss
Topaz concentrate	35.89	48.19	0.13	0.10	0.19	0.39	—	15.11
Wollastonite	46.98	0.10	49.42	1.22	—	0.04	0.13	2.11

TABLE 2

Pigment	Mass content, %			Mass content of chromophore oxides, %				
	CaO · SiO ₂	MgO	SiO ₂	NiO	CoO	CuO	Fe ₂ O ₃	Cr ₂ O ₃
KhP	53.7	18.5	27.8	—	—	—	—	—
1D – 4D	51.3 – 46.4	12.4 – 0.0	26.5 – 24.0	9.8 – 29.6	—	—	—	—
5D – 8D	52.9 – 48.2	16.4 – 5.0	27.3 – 25.0	—	3.4 – 21.8	—	—	—
9D – 11D	50.9 – 47.7	12.3 – 4.9	26.4 – 24.7	—	—	10.4 – 22.7	—	—
12D – 15D	50.9 – 38.7	15.8 – 4.0	26.3 – 20.0	—	—	—	7.0 – 37.3	—
16D – 19D	51.1 – 39.4	15.9 – 4.1	26.4 – 20.4	—	—	—	—	6.7 – 36.1

TABLE 3

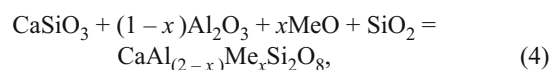
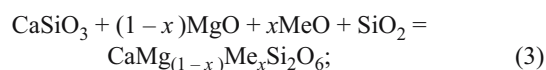
Pigment	Mass content, %			Mass content of chromophore oxides, %				
	CaO · SiO ₂	MgO	SiO ₂	NiO	CoO	CuO	Fe ₂ O ₃	Cr ₂ O ₃
KhP	41.7	36.7	21.6	—	—	—	—	—
1A – 4A	43.0 – 46.4	26.5 – 0.0	22.3 – 24.0	8.2 – 29.6	—	—	—	—
5A – 8A	42.1 – 44.8	33.4 – 11.8	21.8 – 23.2	—	2.7 – 20.3	—	—	—
9A – 11A	42.8 – 44.3	26.3 – 11.7	22.1 – 22.9	—	—	8.8 – 21.1	—	—
12A – 15A	40.9 – 36.4	32.4 – 9.6	21.1 – 18.8	—	—	—	5.6 – 35.2	—
16A – 19A	41.0 – 37.1	32.4 – 9.8	21.2 – 19.2	—	—	—	—	5.4 – 34.0

the activation energy of switching bonds, which enables diffusion processes to proceed under decreased temperatures [3]. The mineralizing effect of topaz should be manifested via the fluoride ions of the gaseous phase released in the decomposition of topaz, whereas boric acid participates in the formation of a liquid phase. The amount of the liquid phase, as a rule, is scarce, and, therefore, the diffusion of liquid in the reaction mixture is limited as well. At the same time, the gaseous phase easily diffuses across the entire volume facilitating the mineralization process and intensifying the reactions.

The main raw materials for producing pigments were natural wollastonite (concentrated) from the Slyudyanskoe deposit, as well as magnesium, silicon, and aluminum oxides. The chemical composition of Slyudyanskoe wollastonite is shown in Table 1; the content of the mineral in the rock is 95 – 97%. X-ray phase and chemical analysis points to a high degree of purity in the rock.

To obtain pigments, wollastonite was mixed with the respective oxides to a stoichiometric diopside or anorthite composition, in accordance with reactions (1) and (2). Chromophores were introduced as water-soluble salts in the amount of 2.7 – 37.3% (here and elsewhere wt.%) converted to oxides. Wollastonite-based compositions with the diopside and anorthite structures are shown in Tables 2 and 3.

It is assumed that the substitution process occurs according to the following reactions:



where $x = 0.1, 0.3, 0.5$, and 0.7 moles.

A parallel experiment was carried out: different mineralizers, namely, topaz concentrate from the Kopna deposit with a mineral content of 90.3% (chemical composition indicated in Table 2) and boric acid in an amount of 2%, were added to mixtures of identical compositions.

Salt solutions were added to initial component mixtures, after which they were dried and fired at 1100 – 1200°C. The obtained cake was milled to a residue not more than 0.2% on a No. 0063 sieve.

Ceramic pigments of a wide color range were synthesized. As was expected, the mineralizing effect of topaz and boric acid is different. At 1100 – 1150°C topaz has an obvious advantage. Pigments containing cobalt have a very bright lilac-pink, sky-blue, or ultramarine tint (especially with low concentrations of CoO), chrome imparts lettuce-green and

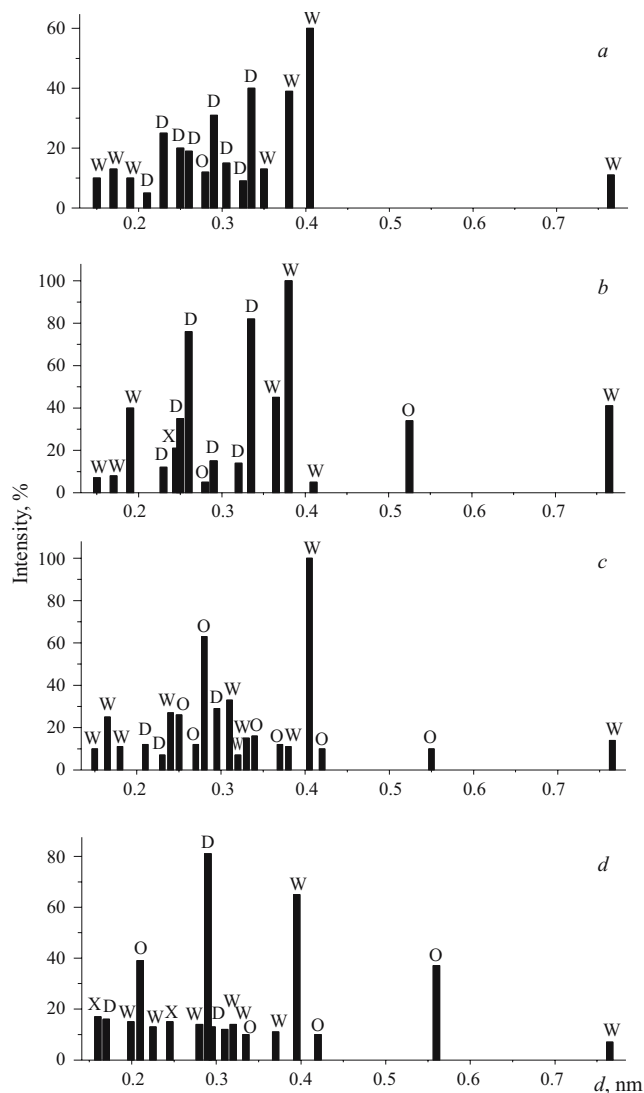


Fig. 1. X-ray diffraction patterns of blank sample (*a, c*) and pigment DT-17 (*b, d*) obtained in reactions (1) and (3) with additives of topaz (*a, b*) and boric acid (*c, d*): W) wollastonite; D) diopside; O) okermanite; X) Cr_2O_3 .

grassy-green shades to pigments, and pigments with Fe_2O_3 have bright orange-sandy, red-brown, or chocolate-brown

TABLE 4

Pigment	Mineralizer: boric acid	Pigment	Mineralizer: topaz
4DB	Light olive	4DT	Green
12DB	Bright yellow-brown	12DT	Brown-orange
16DB	Light olive	16DT	Light brown
1AB	Greenish-light blue	1AT	Light turquoise
5AB	Light blue	5AT	Light ultramarine
6AB	Gray-blue	6AT	Bright blue
12AB	Light brown	12AT	Light apricot
13AB	Red-brown	13AT	Light chocolate brown
16AB	Grayish pink	16AT	Light greenish
17AB	Light gray-green	17AT	Light green
19AB	Green	19AT	Grassy-green

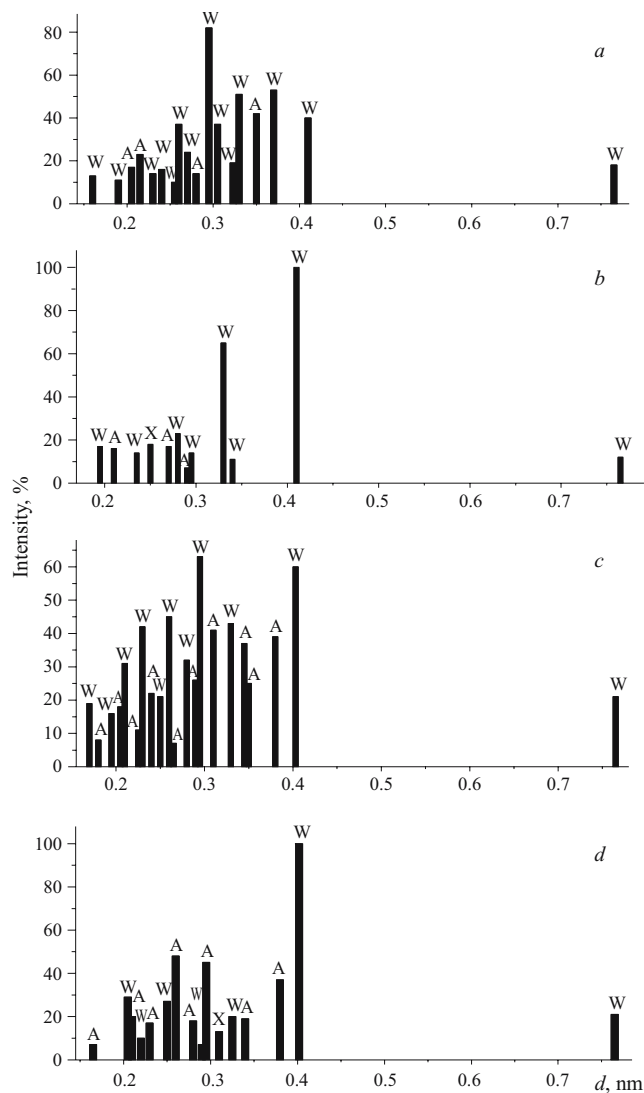


Fig. 2. X-ray diffraction patterns of blank sample (*a, c*) and pigment AT-17 (*b, d*) obtained in reactions (2) and (4) with additives of topaz (*a, b*) and boric acid (*c, d*): W) wollastonite; A) anorthite; X) Cr_2O_3 .

shades. The colors of wollastonite-based pigments at a firing temperature of 1100°C are listed in Table 4.

The brightest color range has been obtained at a temperature of 1100°C. Increasing firing temperature impairs the color characteristics of pigments. X-ray phase analysis indicates that pigments with topaz synthesized according to reactions (1) and (3) at 1100°C exhibit well-defined diopside peaks (Fig. 1). A black test with boric acid mainly forms not a diopside, but an okermanite structure, although diopside and wollastonite peaks are present as well. When chromophores are added, the intensity of the diffraction peaks of diopside grows.

In reactions (2) and (4) both mineralizing additives yield nearly similar results (Fig. 2). At a temperature of 1100°C, x-ray diffraction patterns have both anorthite and wollastonite peaks. As the temperature grows to 1200°C, wollastonite

TABLE 5

Pigment	Chromaticity coordinates		Wavelength, nm	Color purity, %
	<i>X</i>	<i>Y</i>		
6AT	0.21	0.21	477	25
5AB	0.26	0.27	479	15
16DT	0.44	0.42	581	67
12DB	0.45	0.40	586	65

peaks decrease up to disappearance, whereas anorthite peaks increase both in the blank sample and in samples with chromophore additives.

Spectrophotometric analysis (a SF-18 spectrophotometer) identified the spectral reflection curves of the pigments. The chromaticity coordinates *X*, *Y*, and *Z* were calculated based on the reflection curves. The color triangle was used to determine the dominant wavelength and color purity for all pigments. Some results are given in Table 5.

The study has demonstrated that using topaz as a mineralizer in the production of ceramic pigments based on natu-

ral materials is promising, since it improves the color properties of ceramic pigments and lowers the temperature of their synthesis.

An obvious advantage of topaz over the traditional mineralizer (boric acid) has been established. The mineralizing effect of topaz is determined by the intense influence of fluoride ions of the gaseous phase realized in its decomposition, which ensured an enhanced reaction capacity of the mixture in the entire volume. The resulting ceramic pigments have good chromophore properties, are resistant at high firing temperatures, and can be widely used in ceramic production.

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